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THE REPRODUCIBILITY OF THE MERCURY BOILING POINT. THE EFFECT OF PRESSURE ON THE MERCURY BOILING POINT

By James A. Beattie, B. Edwin Blaisdell, and Joseph Kaminsky

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1. Introduction

A comparison of the International Temperature Scale with the absolute scale indicates that the accepted value for the normal sulphur boiling point (444.6° C.) is 0.09° C. too low. If the sulphur point is taken to be 444.69° C., the temperature computed from the Callendar equation is lower than the absolute temperature between the steam and sulphur points, the difference being a maximum of 0.05° C. at 300° C. In the range from 100° C. to 500° C., the scale of the platinum resistance thermometer can be brought into agreement with the absolute scale within the experimental error incident to the use of gas thermometers by computing the temperature t indicated by a platinum resistance thermometer from a cubic equation:

$$t = \frac{R_t - R_0}{\alpha R_0} + \delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right) - \gamma\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)\left(\frac{t}{t_s} - 1\right) \quad (1)$$

where R_t is the resistance at $t°$, R_0 the resistance at the ice point, t_s the absolute temperature of the sulphur point, (444.69°) and α, δ, and γ are constants determined by calibration at the steam and sulphur points and at a point between these two. The values of α, δ, and γ

are of the order of 0.00391, 1.49, and 0.020, respectively. Moser[1] has suggested such a formula to be used to the melting point of gold (1063° C.) the value of γ being of the order of -0.004. This would make the discrepancy between the platinum scale and the absolute scale greater in the range 100° to 450° C. but not much greater since his value of γ is small.

We suggest that the boiling point of mercury be used as a fourth calibration point. Mercury is easily prepared in a pure state and its vapor is much heavier than air so that it can be boiled in an apparatus similar to that used for sulphur. We have found that the mercury point can be reproduced with a probable error of 0.0010° C. The equation for the temperature t_p (°C. Int.) of equilibrium between mercury and its saturated vapor at a pressure p standard mm. is

$$t_p = 356.580 + 0.0730951\,(p - 760) - 0.000\,039866\,(p - 760)^2 + 0.000\,000\,03191\,(p - 760)^3 \quad (2)$$

for the pressure range 660 to 860 mm.

It is often desired to use a platinum thermometer for reproducing the International Temperature Scale at temperatures above the ice point but far below the sulphur boiling point. The value of the thermometer constant δ in the Callendar equation can be determined at the mercury point as well as at the sulphur point.

2. Apparatus and Materials

Thermometry. The platinum resistance thermometers, Nos. 107 and 308, were the same as those used in the work on the sulphur[2] and steam points.[3]

A new Wheatstone bridge made by The Eppley Laboratories, Inc., was used. This bridge was of the Mueller type but had some innovations. The ratio of the resistances of the ratio arms was remarkably constant, varying from 1 to 1.000 001 over a period of a year and the "zero balance" was less than 0.000 02 ohms. The bridge was calibrated in terms of one of the 100-ohm coils. The resistance of each thermometer at the ice point was about 0.01 ohm less on the new bridge. This is to be expected as we made no attempt to calibrate the two bridges in terms of the same standard. This difference should

[1] H. Moser, Wiss. Abh. der Phys.-Tech. Reichsanstalt, **14,** 332 (1930–1931).

[2] J. A. Beattie, Manson Benedict, and B. Edwin Blaisdell, Proc. Am. Acad. Arts and Sci., **71,** 327 (1936).

[3] J. A. Beattie and B. Edwin Blaisdell, Proc. Am. Acad. Arts and Sci., **71,** 361 (1936).

have no effect on the computed temperature or on α and δ. The thermometers were recalibrated at the steam and sulphur points: for No. 107 α had decreased by 0.000 000 019 and δ decreased by 0.000 30; for No. 308 α had increased by 0.000 000 015 and δ decreased by 0.000 04. At the normal mercury point (356.58° C.) the new values of α and δ computed a temperature 0.0012° C. lower for No. 107 and 0.0018° C. lower for No. 308 than that computed by the old constants. The change of the thermometer constants with time could account for such a difference (about six months had elapsed since the work on the steam point).

Barometry. The barometer, comparator, scale, and manostat were the same as those used in the work on the sulphur and steam points. The manostat was filled with helium. Nitrogen could have been used.

Boiling Apparatus. The heating and insulating units, the boiling tube, the protection tube and the radiation shields were identical in dimension with those used in the standard procedure of the sulphur work (see Fig. 2 of reference 2). The protection tube and the two radiation shields and radiation disk were made of steel. The exposed portion of the boiling tube was cooled by a current of air from an electric fan.

Mercury tends to superheat and then boil violently, thus causing a pressure fluctuation. This "bumping" was effectively prevented by the introduction of a large coil of tungsten wire and several pieces of tungsten wire with sharp edges into the boiling tube. Furthermore the level of the liquid in the boiling tube was reduced so that it stood 2 cm. above the top of the heating unit. (This distance was 5 cm. when sulphur was used.)

Mercury. The mercury was purified by electrolysis in a dilute solution of nitric acid and by three distillations, twice in a current of air at 20 mm. pressure and once in vacuo.

3. Experiment Procedure and Corrections

The experimental procedure was the "standard procedure" used in the study of the sulphur point, except that the insulating unit was heated to 300° C. instead of to 400° C., and the level of the liquid was 2 cm. above the top of the heating unit.

The corrections to the measured resistances and the observed pressures were made in the same manner as in the sulphur work. The value of r_1, the ratio of the density of saturated mercury vapor to the density of liquid mercury, is given in Table I. It is computed on the basis that saturated mercury vapor is an ideal monatomic gas. An

error of 1% in r_1 affects the corrected pressure by about 0.001 mm. Smith and Menzies[4] determined the density of saturated mercury vapor over the temperature range 360° to 400° C. with an accuracy of ± 2% and state that the vapor density was "normal" within 1%; Jewett[4] found that the density of the saturated vapor followed the ideal gas law to ± 1% to 325° C.

TABLE I

VALUES OF THE RATIO (r_1) OF THE DENSITY OF SATURATED MERCURY VAPOR AT THE SATURATION PRESSURES p TO THE DENSITY OF LIQUID MERCURY

$$r_1 = \frac{200.61}{82.06 \times 13.5951 \times 760} \frac{p}{(t + 273.1)}$$

$$t = 356.58 + 0.0731\,(p - 760) - 0.000\,040\,(p - 760)^2 + 0.000\,000\,03\,(p - 760)^3$$

p (mm.)	$r_1 \times 10^6$	p (mm.)	$r_1 \times 10^6$	p (mm.)	$r_1 \times 10^6$
660	251	730	275	800	299
670	255	740	279	810	303
680	258	750	282	820	306
690	261	760	286	830	309
700	265	770	289	840	313
710	268	780	292	850	316
720	272	790	296	860	320

4. EFFECT OF VARIATION OF CONDITIONS ON THE INDICATED TEMPERATURE

The standard procedure may be summarized as follows: height of condensation line of mercury above top of insulating unit, 2 cm.; distance from top of insulating unit to mid-point of thermometer coil, 33 cm.; liquid level 2 cm. above top of heating unit; protection tube, steel; temperature of insulating unit 300° C.; method of shielding, two steel radiation shields and a steel radiation disk; boiling tube, 4.2 cm. inside diameter.

An extensive study of the effect of a variation in each of the above conditions was made at the sulphur point. A somewhat less comprehensive investigation at the mercury point may be summarized as follows:

[4] A. Smith and A. W. C. Menzies, J. Am. Chem. Soc., **32**, 1549 (1910); F. B. Jewett, Phil. Mag., (6) **4**, 546 (1902).

(1). Variations in the current input in the heater sufficient to change the height of the condensation line above the top of the insulating unit from 0.5 to 6.0 cm. was without effect greater than 0.001° C. on the indicated temperature. No progressive effect was noticeable.

(2). A variation of 10 cm. in the depth of immersion of the thermometer had a maximum effect of 0.001° C.

(3). When no current was passed through the insulating unit the temperature read in three separate pairs of determinations was + 0.0009°, − 0.0017°, and + 0.0006° C. higher than when the insulating unit was heated to 300° C.

The method of shielding had been thoroughly studied at the sulphur point, and the results given in paragraph (3) above show that the shielding was adequate. Within our experimental error of a determination—0.0010° C.—variations in our standard procedure were without effect on the indicated temperature.

5. Normal Boiling Point of Mercury

Five determinations of the normal boiling point of mercury were made with thermometer No. 107 and six with thermometer No. 308. In each case the pressure was within 1 mm. of 760 mm., and the temperatures were reduced to 760 mm. by Eq. (2). In addition each of the four runs of Table III leads to a value for the normal mercury point with a weight of about five determinations. These values are listed in Table II. The average value is 356.580 ± 0.002° C. (Int.). The absolute temperature of the normal mercury point is 356.66 ± 0.02° C. The values given in International Critical Tables[5] for the normal boiling point of mercury are 356.90° and 356.70° C., which are presumably on the International Temperature Scale.

TABLE II

The Normal Boiling Point of Mercury

Average of 5 determinations with therm. No. 107	356.5779 °C. (Int.)
Average of 6 determinations with therm. No. 308	356.5795
Value from run No. 1 (therm. No. 308)	356.5813
Value from run No. 2 (therm. No. 308)	356.5823
Value from run No. 3 (therm. No. 107)	356.5779
Value from run No. 4 (therm. No. 107)	356.5810
Average	356.5800 ± 0.0016

[5] International Critical Tables, Vol. I, p. 102 (1936); Vol. III, p. 205 (1928).

6. Effect of Pressure on the Mercury Boiling Point

Four runs each consisting of from 8 to 10 determinations covering the pressure range 660 to 860 mm. were made to study the effect of pressure on the mercury point. The results are given in Table III.

At the steam and the sulphur points we adjusted α and δ, respectively, in such a manner as to make the temperature pass through the accepted normal boiling point at one standard atmosphere for each run. Such an adjustment in α or δ raises every calculated temperature by the same absolute amount within 0.0002° C. For the mercury

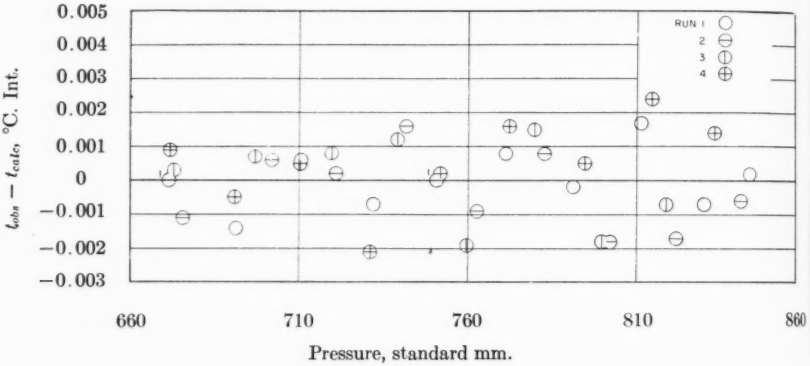

Figure 1. Plot of the observed temperatures minus the temperatures calculated by Eq. (2) against the pressure.

point we added a constant value Δ to each determination of a given run in order to make the average of the four or five determinations nearest 760 mm. as corrected by Eq. (2) to 760 mm. give our accepted value 356.580° C. for the normal boiling point. The computation of Δ for each run is given in Table IV. This process required several approximations in order that all values be consistent to 0.0001° C., as was also true of the work on the sulphur and steam points.

The final equation for the temperature t_p of equilibrium between liquid mercury and its saturated vapor at a pressure p standard mm. for the pressure range 660 to 860 mm. is:

$$t_p = 356.580 + 0.0730951\,(p - 760) - 0.000\,039866\,(p - 760)^2 + 0.000\,000\,03191\,(p - 760)^3. \quad (2)$$

The three constants were determined by the method of least

TABLE III

THE EFFECT OF PRESSURE ON THE MERCURY POINT

$$t_{calc} = t_p = 356.580 + 0.0730951\,(p - 760) - 0.000\,039866\,(p - 760)^2 + 0.000\,000\,03191\,(p - 760)^3$$

$$t_{obs} = \frac{R_t - R_0}{R_0\alpha} + \delta\left(\frac{t_{obs}}{100}\right)\left(\frac{t_{obs}}{100} - 1\right) + \Delta$$

Run No.	Determination No.	Barometer	Pressure Standard mm.	Thermometer No.	R_t	R_0, α, δ, Δ	t_{obs}, °C. Int.	$(t_{obs} - t_{calc}) \times 10^3$ °C. Int.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	150	Left	671.479	308	59.78986	25.76471	349.7750	0.0
	151		691.469		59.93674	0.003921708	351.3718	−1.4
	152		710.604		60.07437	1.49172	352.8689	+0.6
	153		731.991		60.22425	−0.0013	354.5000	−0.7
	154		750.623		60.35201		355.8911	0.0
	155		771.207		60.49006		357.3950	+0.8
	156		791.105		60.62043		358.8158	−0.2
	157		811.329		60.75039		360.2329	+1.7
	158		829.984		60.86751		361.5105	−0.7
	159		843.762		60.95285		362.4418	+0.2
2	160	Left	840.974	308	60.93560	25.76466	362.2538	−0.6
	161		821.803		60.81621	0.003921708	360.9511	−1.7
	162		802.385		60.69298	1.49172	359.6071	−1.8
	163		782.642		60.56536	−0.0023	358.2158	+0.8
	164		762.725		60.43341		356.7780	−0.9
	165		741.791		60.29194		355.2372	+1.6
	166		721.002		60.14770		353.6671	+0.2
	167		702.092		60.01359		352.2079	+0.6
	168		675.605		59.82037		350.1069	−1.1

TABLE III—(*Continued*)

THE EFFECT OF PRESSURE ON THE MERCURY POINT

Run No.	Determination No.	Barometer	Pressure Standard mm.	Thermometer No.	R_t	R_0, α, δ, Δ	t_{obs}, °C. Int.	$(t_{obs}-t_{calc})\times 10^3$ °C. Int.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
3	169	Left	672.946	107	58.20970	25.08078	349.8939	+0.3
	170		696.913		58.38058	0.003921359	351.8027	+0.7
	171		719.812		58.53930	1.49221	353.5768	+0.8
	172		739.173		58.67025	+0.0021	355.0413	+1.2
	173		759.902		58.80696		356.5709	−1.9
	174		779.616		58.93464		358.0002	+1.5
	175		799.914		59.06268		359.4342	−1.8
	176		818.766		59.17955		360.7436	−0.7
	177		839.988		59.30698	Pressure in error by 0.2 mm.		
4	178	Left	832.922	107	59.26605	25.08071	361.7120	+1.4
	179		814.471		59.15353	0.003921359	360.4508	+2.4
	180		794.635		59.02990	1.49221	359.0657	+0.5
	181		772.288		58.88774	−0.0010	357.4738	+1.6
	182		751.894		58.75472		355.9850	+0.1
	183		731.087		58.61575		354.4304	−2.1
	184		710.533		58.47559		352.8633	+0.5
	185		690.946		58.33851		351.3314	−0.5
	186		671.853		58.20196		349.8062	+0.9
							Average deviation	1.0

squares. The deviations of the values calculated by Eq. (2) from the observed values (column (8) of Table III) are given in column (9) of Table III. These deviations are plotted against the pressure in Fig. 1. The average deviation of the observed temperatures from those computed by Eq. (2) is $\pm$ 0.0010° C.

TABLE IV

Computation of Δ

$$\Delta = t_p - \left[\frac{R_t - R_0}{\alpha R_0} + \delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)\right] = t_p - t_{therm.}$$

(See Table III for the data used)

Run No.	Determination No.	t_p	$t_{therm.}$	Δ
1	153	354.5007	354.5013	−0.0006
	154	355.8911	355.8924	− .0013
	155	357.3942	357.3963	− .0021
	156	358.8160	358.8171	− .0011
			Δ for run No. 1	− .0013
2	162	359.6089	359.6094	− .0005
	163	358.2150	358.2181	− .0031
	164	356.7789	356.7803	− .0014
	165	355.2356	355.2395	− .0039
	166	353.6669	353.6694	− .0025
			Δ for run No. 2	− .0023
3	171	353.5760	353.5747	+ .0013
	172	355.0401	355.0392	+ .0009
	173	356.5728	356.5688	+ .0040
	174	357.9987	357.9981	+ .0006
	175	359.4360	359.4321	+ .0039
			Δ for run No. 3	+ .0021
4	180	359.0652	359.0667	− .0015
	181	357.4722	357.4748	− .0026
	182	355.9849	355.9860	− .0011
	183	354.4325	354.4314	+ .0011
			Δ for run No. 4	− .0010

We wish to thank the National Research Council for a grant from the Grants-in-Aid and the American Academy of Arts and Sciences for a grant from the Permanent Science Fund.

7. Summary

The temperature of equilibrium between liquid mercury and its saturated vapor is suggested as a fourth calibration point in the temperature range 0° to 500° C. When the four fixed points (ice, steam, mercury, sulphur) are used and a cubic equation employed, the temperatures computed from the resistance of a platinum thermometer ageee with the absolute temperature within the accuracy of determination of the latter over the temperature range 0° to 500° C. The use of three fixed points (ice, steam, mercury) and the ordinary Callendar quadratic equation is convenient when temperatures on the International Scale up to 350° C. are to be measured.

The mercury point can be reproduced with a probable error of 0.0010° C. in an apparatus identical with that used for realizing the sulphur point.

The equation for the temperature t_p of equilibrium between liquid mercury and its vapor at a pressure p standard mm. from 660 to 860 mm. is

$$t_p = 356.580 + 0.0730951\ (p - 760) - 0.000\,039866\ (p - 760)^2 + 0.000\,000\,03191\ (p - 760)^3.$$

where t_p is on the International Temperature Scale. The average deviation of 36 determinations from the equation is $\pm$ 0.0010° C.

The normal boiling point of mercury on the absolute temperature scale is 356.66 $\pm$ 0.02° C.

8. Appendix

Effects of Errors in the Determination of R_t, R_0, α, and δ on the Computed Temperature in the Neighborhood of the Mercury Point. In Table V are given the errors in the temperature computed from the Callendar Equation due to errors in the determination of the resistance of the thermometer R_t and in the thermometer constants R_0, α, δ for several temperatures in the neighborhood of the mercury point. This table is similar to those given for the sulphur and steam points.

TABLE V

EFFECT OF ERRORS IN THE DETERMINATION OF R_t, R_0, α, δ ON THE TEMPERATURE COMPUTED FROM THE CALLENDAR EQUATION IN THE NEIGHBORHOOD OF THE MERCURY POINT

$$\Delta t = \frac{\Delta R_t}{R_0 \alpha D} \qquad \Delta t = -\frac{(R_t - R_0)\,\Delta\alpha}{R_0 \alpha^2 D} \qquad \Delta t = (1 - D)\Delta t^*$$

$$\Delta t = -\frac{R_t \Delta R_0}{R_0^2 \alpha D} \qquad \Delta t = \left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)\frac{\Delta\delta}{D} \qquad D = 1 - \left(\frac{2t}{100} - 1\right)\frac{\delta}{100}$$

Assumed constants: $R_0 = 25.09081$ $\alpha = 0.003921378$ $\delta = 1.49251$
Assumed variations: $R_t = R_0 = 0.00010$ $\Delta\alpha = 0.000000010$ $\Delta\delta = 0.00010$
$\Delta t = 0.0010^*$

Temperature (°C. Int.)	Error × 10^3 (°C.) in Computed Temperature due to				
	ΔR_t	ΔR_0	$\Delta\alpha$	$\Delta\delta$	Δt^*
364.58	1.122	−2.662	−0.986	1.065	0.094
360.58	1.120	−2.643	− .974	1.036	.093
356.58	1.119	−2.623	− .963	1.007	.092
352.58	1.117	−2.604	− .951	0.979	.090
348.58	1.116	−2.584	− .940	0.951	.089

*This equation and column give the effect on t produced by a variation in the temperature substituted into the term $\delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)$.